AD-A155 038 OVERLAP INTÉGRALS FOR ATOM-METAL SURFACE INTERACTIONS 1/1
(U) ROCHESTER UNIV NY DEPT OF CHEMISTRY
W C MURPHY ET AL. MAY 85 TR-67 N00014-80-C-0472

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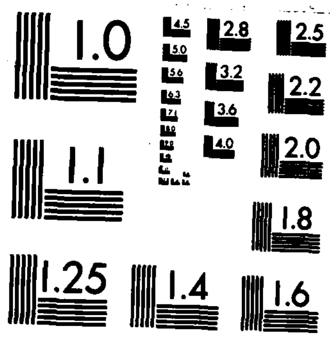

MICROCOPY RESOLUTION TEST CHART
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Contract N00014-80-C-0472

Task No. NR 056-749

TECHNICAL REPORT No. 67

Overlap Integrals for Atom-Metal Surface Interactions

by

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AD-A155 038

Prepared for Publication

in

International Journal of Quantum Chemistry

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May 1985

85 5 23 137

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) UROCHESTER/DC/85/TR-67	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION Department of Chemistry University of Rochester 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research (Code 413)
6c. ADDRESS (City, State and ZIP Code) River Station Rochester, New York 14627	7b. ADDRESS (City, State and ZIP Code) Chemistry Program 800 N. Quincy Street Arlington, Virginia 22217
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract N00014-80-C-0472
8c. ADDRESS (City, State and ZIP Code) Chemistry Program 800 N. Quincy Street Arlington, Virginia 22217	10. SOURCE OF FUNDING NOS. PROGRAM ELEMENT NO.: 61153N PROJECT NO.: 013-08 TASK NO.: NR 056-748 WORK UNIT NO.:

11. TITLE
Overlap Integrals for Atom-Metal Surface Interactions

12. PERSONAL AUTHOR(S)
William C. Murphy and Thomas F. George

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Yr., Mo., Day)	15. PAGE COUNT
Interim Technical	FROM ______ TO ______	May 1985	16

16. SUPPLEMENTARY NOTATION
Prepared for publication in International Journal of Quantum Chemistry

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB. GR.	OVERLAP INTEGRALS; EXACT ALGEBRAIC EXPRESSIONS; TRIPLE INTEGRALS; ZERO PARALLEL WAVEVECTOR; ATOM-METAL SURFACE; GENERAL CASE

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Atom-metal surface overlap integrals are of utmost importance in surface energy calculations. Direct numerical evaluation of these triple integrals can be very time consuming. However, we have developed an exact algebraic expression, where formulas for the coefficients are given for both the general case and the special case where the parallel wavevector is zero. Some numerical examples of the overlap for H on Al are given.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☒ DTIC USERS ☐	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. David L. Nelson	22b. TELEPHONE NUMBER (Include Area Code) (202)696-4410 22c. OFFICE SYMBOL

DD FORM 1473, 83 APR EDITION OF 1 JAN 73 IS OBSOLETE.

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

International Journal of Quantum Chemistry, in press

OVERLAP INTEGRALS FOR ATOM-METAL SURFACE INTERACTIONS

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Abstract

Atom-metal surface overlap integrals are of utmost importance in surface energy calculations. Direct numerical evaluation of these triple integrals can be very time consuming. However, we have developed an exact algebraic expression, where formulas for the coefficients are given for both the general case and the special case where the parallel wavevector is zero. Some numerical examples of the overlap for H on Al are given.

Additional keywords: wave functions,

A-1

1. Introduction

The interaction of an adatom with a metal surface is of utmost importance in surface physics (and surface science in general). Several researchers[1-6] have expended a great deal of effort in its determination. To evaluate this interaction potential, one common method is to first expand the total wavefunction in a mixed basis set,

$$\psi_i(\vec{r}) = \sum_a c_a^i \, \phi_a(\vec{r}) + \sum_k c_k^i \phi_k(\vec{r}) \quad , \tag{1}$$

where $\phi_a(\vec{r})$ are wavefunctions that are localized on the adatom with quantum number a, and $\phi_k(\vec{r})$ are the delocalized wavefunctions of the metal with quantum number k. One of the difficulties involved with such an expansion is the need to remove the overcompleteness. Lundqvist[4] has suggested that this can best be done by the requirement

$$\sum_k c_k^i \, S_{a,k} = 0 \quad , \tag{2}$$

where the overlap integral is given by

$$S_{a,k} = \langle a|k\rangle \quad . \tag{3}$$

Consequently, a knowledge of this overlap is needed to remove the overcompleteness. Furthermore, to solve the secular determinant for Eq. (1), one needs to know the values of the overlap integral and two interaction integrals. The interaction integrals in turn can be related to each other and the overlap via the Hermitian property

$$E_a \, S_{k,a}^* + \langle k|V_L|a\rangle^* = E_k \, S_{a,k} + \langle a|V_a|k\rangle \quad , \tag{4}$$

where E_a and V_a are the eigenvalue and potential of the isolated atom, and E_k and V_L are the eigenvalue and potential of the isolated metal. Consequently, an evaluation of the overlap is vital for solving the secular deteminant.

In this paper, we show that a closed form expression for the overlap can be obtained. We define our system in the next section, and following this we give the details of evaluating $S_{a,k}$. Finally, \ ; discuss our results and suggest further uses of this calculation.

2. The System

We shall examine the case of a single atom impinging on a simple metal surface. The electrons associated with the atom will be approximated by Slater orbitals,[7]

$$\phi_a(\vec{r}) = \left[\frac{(2\xi)^{2n+1}}{(2n)!}\right]^{1/2} r^{n-1}\ e^{-\xi r}\ Y_\ell^m(\theta,\phi) \quad , \tag{5}$$

where $Y_\ell^m(\theta,\phi)$ are the spherical harmonics, $a\equiv(n,\ell,m)$ are the atomic quantum numbers, and ξ is the orbital factor. The origin of our system is chosen to be on the surface; therefore,

$$r = \sqrt{r_{\parallel}^2 + (z-z_a)^2} \quad , \tag{6}$$

where z and $r_{\parallel}$ are the position of the electron perpendicular and parallel to the surface, and z_a is the distance of the atom from the surface. The Slater orbital choice was made for computational efficiency. Furthermore, if V_a is Coulombic, the interaction integral for the atomic potential will be

$$\langle a|V_a|k\rangle = \frac{2\xi Z}{\sqrt{(2n)(2n-1)}}\ S_{a',k} \quad , \tag{7}$$

where Z is the nuclear charge and $a' = (n-1,\ell,m)$. Consequently, all integrals of interest can be written in terms of the overlap.

Previously, the metal has been modeled within the truncated jellium approximation.[1-5] Instead of using the numerical wavefunctions from this model, we shall consider the metal electrons as particle-in-a-box. Such wavefunctions are good approximations to the jellium model and provide the basis set necessary for a more exact approach within the nearly-free-electron approximation.[8] These particles-in-a-box wavefunctions are

$$\Phi_k(\vec{r}) = A_s^{-1/2} e^{i\vec{k}_{\parallel}\cdot\vec{r}} f(z) \quad , \tag{8}$$

where A_s is the surface normalization area, and $k_{\parallel}$ is the component of the electronic wavevector parallel to the surface. $f(z)$ is the one-dimensional particle-in-a-box wavefunction:

$$f(z) = \left(\frac{2}{L}\right)^{1/2} \sin(k_z z + \theta_k) \tag{9a}$$

for $-L < z < 0$,

$$f(z) = \left(\frac{2}{L}\right)^{1/2} \sin\theta_k \, e^{-qz} \tag{9b}$$

for $z > 0$, and

$$f(z) = \left(\frac{2}{L}\right) \sin(-k_z L + \theta_k) \, e^{q(z+L)} \tag{9c}$$

for $z < -L$, with

$$q = \sqrt{2W - k_z^2} \tag{10}$$

$$\tan\theta_k = -\frac{k_z}{q} \quad , \tag{11}$$

where L is the thickness of the metal, k_z is the component of the electronic wavevector perpendicular to the surface, and W is the sum of the work function and the Fermi energy.

To calculate the overlap of the wavefunctions given in Eqs. (5) and (8), we must solve the integral

$$S_{a,k} = A_s^{-1/2}\left[\frac{(2\xi)^{2n+1}}{(2n)!}\right]^{1/2} \int d\vec{r}\; r^{n-1}\; e^{-\xi r}\; Y_\ell^{m*}(\theta,\phi)\; e^{i\vec{k}_\parallel\cdot\vec{r}}\; f(z+z_a) \quad , \tag{12}$$

where the z_a is needed in the metal wavefunction since our origin is centered on the adatom. At first this integral appears quite complicated, due to the broken symmetry caused by the surface. However, we can carry out an evaluation by means of a Fourier expansion.

3. Evaluation

The metal wavefunction, Eq. (8), can be represented by a Fourier transform,

$$\phi_k(\vec{r}) = \int d\vec{s}\; \phi_k(\vec{s})\; e^{i\vec{s}\cdot\vec{r}} \quad , \tag{13}$$

where $\vec{s}$ is the Fourier coordinate. The transform of the wavefunction is given by

$$\phi_k(\vec{s}) = \frac{f(s_z)}{A_s^{1/2}}\; \delta(\vec{k}_\parallel - \vec{s}_\parallel) \tag{14}$$

with

$$f(s_z) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dz\; e^{is_z z}\; f(z+z_a) \;, \tag{15}$$

where $\delta(\vec{k}_\parallel - \vec{s}_\parallel)$ is the Dirac delta function. Using Eq. (9) in Eq. (15), we obtain

$$f(s_z) = \frac{1}{2\pi}\left(\frac{2}{L}\right)^{1/2}\Big\{\sin\theta_k \int_0^\infty dz\; e^{is_z(z-z_a)}\, e^{-qz}$$

$$+ \sin(\theta_k - k_z L)\int_{-\infty}^{-L} dz\; e^{is_z(z-z_a)}\, e^{q(z+L)} + \int_{-L}^{0} dz\; e^{is_z(z-z_a)} \sin(k_z z+\theta_k)\Big\} \tag{16}$$

Evaluating these integrals is straightforward and gives

$$f(s_z) = \frac{1}{2\pi}\left(\frac{2}{L}\right)^{1/2}\Big\{\frac{i\sin\theta_k\; e^{-is_z z_a}}{s_z + iq} + \frac{i\sin(\theta_k - k_z L)\; e^{-is_z(z_a+L)}}{s_z - iq}$$

$$- \frac{e^{-is_z z_a}}{2}\left[\frac{e^{i\theta_k}}{k_z+s_z} + \frac{e^{-i\theta_k}}{k_z-s_z} - \frac{e^{-i[(k_z+s_z)L+\theta_k]}}{k_z+s_z} - \frac{e^{i[(k_z-s_z)L+\theta_k]}}{k_z-s_z}\right]\Big\} \;. \tag{17}$$

Combining Eqs. (12) and (13), we can express the overlap as

$$S_{a,k} = \left[\frac{(2\xi)^{2n+1}}{(2n)!}\right]^{1/2} \int d\vec{s}\ \Phi_k(\vec{s}) \int d\vec{r}\ r^{n-1}\ e^{-\xi r}\ Y_\ell^{m*}(\theta,\phi)\ e^{i\vec{s}\cdot\vec{r}} \quad . \tag{18}$$

The exponential can be expanded in terms of the spherical harmonics,[9]

$$e^{i\vec{s}\cdot\vec{r}} = 4\pi \sum_{\ell'=0}^{\infty} \sum_{m'=-\ell'}^{\ell'} i^{\ell'}\ Y_{\ell'}^{m'*}(\theta_s,\phi_s) Y_{\ell'}^{m'}(\theta,\phi) j_{\ell'}(sr) \quad , \tag{19}$$

where $j_{\ell'}(sr)$ is the spherical Bessel function. Using this in Eq. (18) and the orthonormality of the spherical harmonics, the overlap reduces to

$$S_{a,k} = \left[\frac{(2\xi)^{2n+1}}{(2n)!}\right]^{1/2} 4\pi i^{\ell} \int d\vec{s}\ \Phi(\vec{s})\ Y_\ell^{m*}(\theta_s,\phi_s) \int dr\ r^{n+1}\ j_\ell(sr)\ e^{-\xi r} \quad . \tag{20}$$

By Eq. (14), this can be further reduced to

$$S_{a,k} = 4\pi i^{\ell} \left[\frac{(2\ell+1)\ (\ell-|m|)!\ (2\xi)^{2n+1}}{4\pi\ (\ell+|m|)!\ (2n)!}\right]^{1/2} A_s^{-1/2}$$

$$\times\ e^{-im\phi_k} \int_{-\infty}^{+\infty} ds_z\ f(s_z)\ P_\ell^{|m|}\left(\frac{s_z}{s}\right) \int dr\ r^{n+1}\ j_\ell(sr)\ e^{-\xi r} \quad , \tag{21}$$

where ϕ_k is the azimuthal angle in k-space, $P_\ell^{|m|}(\frac{s_z}{s})$ is the associated Legendre function, and s is now given by

$$s = \sqrt{k_{\parallel}^2 + s_z^2} \tag{22}$$

The spherical Bessel function can readily be expanded as[10]

$$j_\ell(sr) = \frac{1}{2sr} \sum_{t=0}^{\ell} \frac{i^{t-\ell-1}(\ell+t)!}{t!(\ell-t)!(2sr)^t} \left[e^{isr} + e^{-isr}(-1)^{t-\ell-1}\right] . \tag{23}$$

Using this expression, we can evaluate the inner integral in Eq. (21):

$$S_{a,k} = A_s^{-1/2} e^{-im\phi_k} D \sum_{t=0}^{\ell} \frac{i^{t-1}(\ell+t)!(n-t)!}{t!\,(\ell-t)!}$$

$$\times \int ds_z\, f(s_z)\, P_\ell^{|m|}(\frac{s_z}{s})[\frac{1}{(2s)^{t+1}}][\frac{1}{(\xi-is)^{n-t+1}} + \frac{(-1)^{t-\ell-1}}{(\xi+is)^{n-t+1}}] \quad , \qquad (24)$$

where for convenience, we define

$$D = 4\pi\left[\frac{(2\ell+1)\ (\ell-|m|)!\ (2\xi)^{2n+1}}{4\pi\ (\ell+|m|)!\ (2n)!}\right]^{1/2} \qquad (25)$$

In order to evaluate the integral in Eq. (24), it is easier to examine the integrand with the fractions combined:

$$S_{a,k} = A_s^{-1/2} e^{-im\phi_k} D \sum_{t=0}^{\ell} \frac{i^{t-1}(\ell+t)!\ (n-t)!}{t!\ (\ell-t)!} \int_{-\infty}^{+\infty} ds_z\, f(s_z)\, P_\ell^{|m|}(\frac{s_z}{s})[\frac{1}{(2s)^{t+1}}]$$

$$\times\ \xi^{n-t-1} \sum_{j=0}^{n-t+1} \frac{(n-t+1)!}{(n-t+1-j)!\ j!} (\frac{i}{\xi})^j \frac{[1+(-1)^{t-\ell-1+j}]s^j}{(\xi^2+k_\parallel^2+s_z^2)^{n-t+1}} \quad . \qquad (26)$$

Eq. (26) can be solved by considering the integral as extended over a semicircle in the negative complex plane. The total integral over this enclosed path gives

$$\int_{-\infty}^{+\infty} ds_z \ldots + \int_C ds_z \ldots = -2\pi i \sum_j R_j \quad , \qquad (27)$$

where the integrand is the same as in Eq. (26). The C in the second integral implies integration over the semicircle part of the curve, and R_j are the residues of the poles contained within the total curve. Since the integral is in the negative complex plane, the exponentials in $f(s_z)$ goes to zero at infinity; the second integral vanishes. Consequently, the integral in Eq. (26) only depends on the poles in the negative complex plane. Inspection of the integrand reveals three such poles: (1) a pole of order 1 at $s_z = -iq$ contained in $f(s_z)$; (2) a pole of order n+1 at $s_z = -i\sqrt{\xi^2+k_\parallel^2}$ from the fraction in the sum; and (3) a pole of order ℓ at $s_z = -ik_\parallel$ due partially to the Legendre function and partically to the fraction it multiplies.

Using Eq. (17), we can easily determine the residue at the first pole:

$$R_1 = -\frac{1}{2\pi i}\left(\frac{2}{LA_s}\right)^{1/2} e^{-im\phi_k} D\sin\theta_k e^{-qz_a}\sum_{t=0}^{\ell}\frac{(\ell+t)!\,(n-t)!}{t!\,(\ell-t)!} P_\ell^{|m|}\left(\frac{-q}{\sqrt{q^2-k_{\parallel}^2}}\right)$$

$$\times\frac{1}{\left(2\sqrt{q^2-k_{\parallel}^2}\right)^{t+1}}\left[\frac{1}{\left(\xi+\sqrt{q^2-k_{\parallel}^2}\right)^{n-t+1}}+\frac{(-1)^{t-\ell-1}}{\left(\xi-\sqrt{q^2-k_{\parallel}^2}\right)^{n-t+1}}\right], \quad (28)$$

where we have ignored terms that vanish as the metal thickness, L, becomes large. In order to evaluate the other two residues, we first define

$$F(is_z) = \left[\frac{i\sin\theta_k}{s_z+iq_k} - \frac{1}{2}\left(\frac{e^{i\theta_k}}{k_z+s_z}+\frac{e^{-i\theta_k}}{k_z-s_z}\right)\right]$$

$$\times\sum_{t=0}^{\ell} i^{t-1}\frac{(\ell+t)!\,(n-t)!}{t!(\ell-t)!} P_\ell^{|m|}\left(\frac{s_z}{s}\right)\left[\frac{1}{(2s)^{t+1}}\right]\left[\frac{1}{(\xi-is)^{n-t+1}}+\frac{(-1)^{t-\ell-1}}{(\xi+is)^{n-t+1}}\right]. \quad (29)$$

Consequently, we can now write the residue at $s_z = -i\sqrt{\xi^2+k_{\parallel}^2}$ as

$$R_2 = \frac{1}{2\pi}\left(\frac{2}{LA_s}\right)^{1/2} e^{-im\phi_k}\frac{D}{n!}\frac{d^n}{ds_z^n}\left\{\left[s_z+i\sqrt{\xi^2+k_{\parallel}^2}\right]^{n+1} F(is_z)\, e^{is_z z_a}\right\}_{s=-i\sqrt{\xi^2+k_{\parallel}^2}}. \quad (30)$$

If we let $x = is_z$, then

$$R_2 = -\frac{i}{2\pi}\left(\frac{2}{LA_s}\right)^{1/2} e^{-im\phi_k}\frac{D}{n!}\frac{d^n}{dx^n}\left\{\left[x-\sqrt{\xi^2+k_{\parallel}^2}\right]^{n+1} F(x)\, e^{-xz_a}\right\}_{x=\sqrt{\xi^2+k_{\parallel}^2}}. \quad (31)$$

Using Leibnitz' formula for the differentiation of the product,[11] we obtain

$$R_2 = -\frac{i}{2\pi}\left(\frac{2}{LA_s}\right)^{1/2} e^{-im\phi_k} \frac{D}{n!} \sum_{h=0}^{n} \frac{n!(-1)^{n-h}}{(n-h)!\,h!} z_a^{n-h} e^{-\sqrt{\xi^2+k_\parallel^2}\, z_a}$$

$$\frac{d^h}{dx^h}\left\{\left(x-\sqrt{\xi^2+k_\parallel^2}\right)^{n+1} F(x)\right\}_{x=\sqrt{\xi^2+k_\parallel^2}} \quad . \tag{32}$$

If we now define

$$B_h = \frac{(-1)^{n-h+1} D}{(n-h)!\,h!} \frac{d^h}{dx^h}\left\{ x-\sqrt{\xi^2+k_\parallel^2}^{\;n+1} F(x)\right\}_{x=\sqrt{\xi^2+k_\parallel^2}} \tag{33}$$

we can then write the second residue as

$$R_2 = \frac{i}{2\pi}\left(\frac{2}{LA_s}\right) e^{-im\phi_k} \left(\sum_{h=0}^{n} B_h z_a^{n-h}\right) e^{-\sqrt{\xi^2+k_\parallel^2}\, z_a} \quad . \tag{34}$$

Similarly, we can obtain the residue at $s_z = -ik_\parallel$ as

$$R_3 = \frac{i}{2\pi}\left(\frac{2}{LA_s}\right) e^{im\phi_k} \left(\sum_{h=0}^{\ell-1} C_h z_a^{\ell-1-h}\right) e^{-k_\parallel z_a} \quad . \tag{35}$$

for $\ell > 0$. If $\ell = 0$, there is no residue at $s_z = -ik_\parallel$. The coefficients are given by

$$C_h = \frac{(-1)^{\ell-h} D}{(\ell-1-h)!\,h!} \frac{d^h}{dx^h}\left\{[x-k_\parallel]^\ell F(x)\right\}_{x=k_\parallel} \tag{36}$$

In the spirit of the second and third residues, we can rewrite the first, Eq. (28), as

$$R_1 = \frac{i}{2\pi}\left(\frac{2}{LA_s}\right)^{1/2} e^{-im\phi_k} A\, e^{-qz_a} \quad , \tag{37}$$

where

$$A = D\sin\theta_k \sum_{t=0}^{\ell} \frac{(\ell+t)!(n-t)!}{t!\,(\ell-t)!} P_\ell^{|m|}\left(\frac{-q}{\sqrt{q^2-k_\parallel^2}}\right)\frac{1}{\left(2\sqrt{q^2-k_\parallel^2}\right)^{t+1}}$$

$$\times \left[\frac{1}{\left(\xi + \sqrt{q^2-k_\parallel^2}\right)^{n-t+1}} + \frac{(-1)^{t-\ell-1}}{\left(\xi - \sqrt{q^2-k_\parallel^2}\right)^{n-t+1}} \right] . \quad (38)$$

Since we now have the value of the residue at each pole, we are able to obtain the overla[illegible]

$$S_{a,k} = -2\pi i \sum_{i=1}^{3} R_i \quad , \quad (39)$$

where the minus sign is due to our integrating in the clockwise direction. Using Eqs. (34), (35) and (37), we obtain

$$S_{a,k} = \left(\frac{2}{LA_s}\right)^{1/2} e^{-im\phi_k} \{Ae^{-qz_a} + [\sum_{h=0}^{n} B_h z_a^{n-h}]\, e^{-\sqrt{\xi^2+k_\parallel^2}\, z_a}$$

$$+ [\sum_{h=0}^{\ell-1} C_h z_a^{\ell-1-h}]\, e^{-k_\parallel z_a}\} \quad . \quad (40)$$

Thus, we have reduced the overlap integral to a simple algebraic expression in terms of the distance of the adatom from the surface. Furthermore, as we shall see below, A, B_h and C_h are real; consequently, all imaginary contributions to the overlap are determined by the simple phase factor in Eq. (40).

4. Numeri[illegible] [illegible]edures

In order to [illegible]pute values for the overlap, Eq. (40), one must solve for the coefficients. Th[illegible] procedure for A is straightforward, and its value is given by Eq. (38). B_h and C_h, however, dependent on several differentiations of the function $F(is_z)$. One simplification is obtained by observing that $F(is_z)$ is completely real. This can be shown by making the substitution $x = is_z$ in Eq. (29):

$$F(x) = \left[\frac{\sin\theta_k}{x-q} + \frac{k_z\cos\theta_k - x\sin\theta_k}{x^2+k_z^2}\right] \sum_{t=0}^{\ell} \frac{(\ell+t)!\,(n-t)!}{t!\,(\ell-t)!} P_\ell^{|m|}\left(\frac{-x}{\sqrt{x^2-k_\parallel^2}}\right)$$

$$\times \frac{1}{\left(2\sqrt{x^2-k_\parallel^2}\right)^{t+1}} \left[\frac{1}{\left(\xi + \sqrt{x^2-k_\parallel^2}\right)^{n-t+1}} + \frac{(-1)^{t-\ell-1}}{\left(\xi - \sqrt{x^2-k_\parallel^2}\right)^{n-t+1}}\right]. \qquad (41)$$

To proceed with the evaluation of B_h and C_h, one could obtain a closed-form expression by repeated use of Leibnitz' formula or attempt to use a numerical approach based on finite differences.[12] However, a simplified form of the overlap can be obtained for the special case of $k_\parallel = 0$. Since the overlap would be expected to be greatest for k_z large ($k_\parallel$ small), one could use this special case as a basis for obtaining a general solution.

If we assume that $k_\parallel = 0$, the associated Legendre function in Eqs. (38) and (41) will vanish unless $m = 0$. Consequently, $S_{a,k} = 0$ for $k_\parallel = 0$ and $m \neq 0$. For the case where $m = 0$, to evaluate C_h one must include in Eq. (29) the terms that depend on L from Eq. (17) since these terms do not vanish at $s_z = 0$. However, the value of these terms assures that $F(is_z)$ and, consequently, C_h goes to zero. Therefore, for $k_\parallel = 0$ and $m = 0$, the overlap becomes

$$S_{a,k} = \left(\frac{2}{LA_s}\right)^{1/2} \left\{A\, e^{-qz_a} + \left[\sum_{h=0}^{n} B_h\, z_a^{n-h}\right] e^{-\xi z_a}\right\} , \qquad (42)$$

where A can now be simplified to the form

$$A = D\sin\theta_k \sum_{t=0}^{\ell} \frac{(\ell+t)!\,(n-t)!}{t!\,(\ell-t)!} \frac{(-1)^\ell}{(2q)^{t+1}} \left[\frac{1}{(\xi+q)^{n-t+1}} + \frac{(-1)^{t-\ell-1}}{(\xi-q)^{n-t+1}}\right]. \qquad (43)$$

Furthermore, using Eqs. (33) and (41), B_h reduces to

$$B_h = \frac{(-1)^{\ell-h}}{(n-h)!\ h!} D \sum_{t=0}^{\ell} \frac{(\ell+t)!(n-t)!}{t!\ (\ell-t)!}$$

$$\times \frac{d^h}{dx^h}\left[\left(\frac{\sin\theta_k}{x-q} + \frac{k_z\cos\theta_k - x\sin\theta_k}{x^2+k_z^2}\right)\frac{(\xi-x)^t}{(2x)^{t+1}}\right]_{x=\xi} . \quad (44)$$

Another application of Leibnitz' formula leads to

$$B_h = \frac{(-1)^{\ell-h}}{(n-h)!} D \sum_{t=0}^{(\ell,h)} \frac{(\ell+t)!\ (n-t)!\ (-1)^t}{t!\ (\ell-t)!\ (h-t)!}$$

$$\times \frac{d^{h-t}}{dx^{h-t}}\left[\left(\frac{\sin\theta_k}{x-q} + \frac{k_z\cos\theta_k - x\sin\theta_k}{x^2+k_z^2}\right)\frac{1}{(2x)^{t+1}}\right]_{x=\xi} , \quad (45)$$

where (ℓ,h) implies using either ℓ or h, whichever is smaller.

We have evaluated the overlap integral, Eq. (42), for a variety of interacting orbitals for hydrogen atom on the surface of aluminum, and the results are depicted in Fig. 1. As can be seen from this figure, the overlap becomes large as n becomes large, which is due to the fact that the overlap does not become a maximum until the volume occupied by the electronic wavefunction of the atom approaches the size of the metal. This happens at the point of dissociation, $n \to \infty$.

The peculiar structure of the 2s overlap is caused because $q \approx \xi$, i.e., at the exact point of equality A cancels b_0. Consequently, if the atom is on the surface ($z = 0$), the overlap is zero. For $q < \xi$, the metal surface damping dominates the overlap at small z; for $q > \xi$, the atomic damping dominates.

5. Discussion

We have demonstrated that the overlap integrals for the wavefunctions of an atom with a metal surface can be written as algebraic expressions in term of the distance from the surface. Furthermore, we have shown that these expressions are real except for a simple multiplicative phase factor. Analytical expressions for the coefficients of the overlap formulas have also been presented. Solving these closed-form expressions for the overlaps will be much more computationally efficient than direct numerical solution of the overlap integrals. Since other integrals of interest in surface calculations can be written in terms of the overlaps, this efficiency will be transferred to atom-metal surface potential energy calculations. Such integrals are also extremely useful in studying such problems as atom-surface charge transfer, scattering and energy coupling. These problems are of ongoing interest in our research.

Acknowledgements

This research was supported in part by the Air Force Office of Scientific Research (AFSC), United States Air Force, under Grant AFOSR-82-0046, the Office of Naval Research, and the National Science Foundation under Grant CHE-8320185. The United States Government is authorized to reproduce and distribute reprints for governmental purposes notwithstanding any copyright notation hereon. TFG acknowledges the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Award (1975-86).

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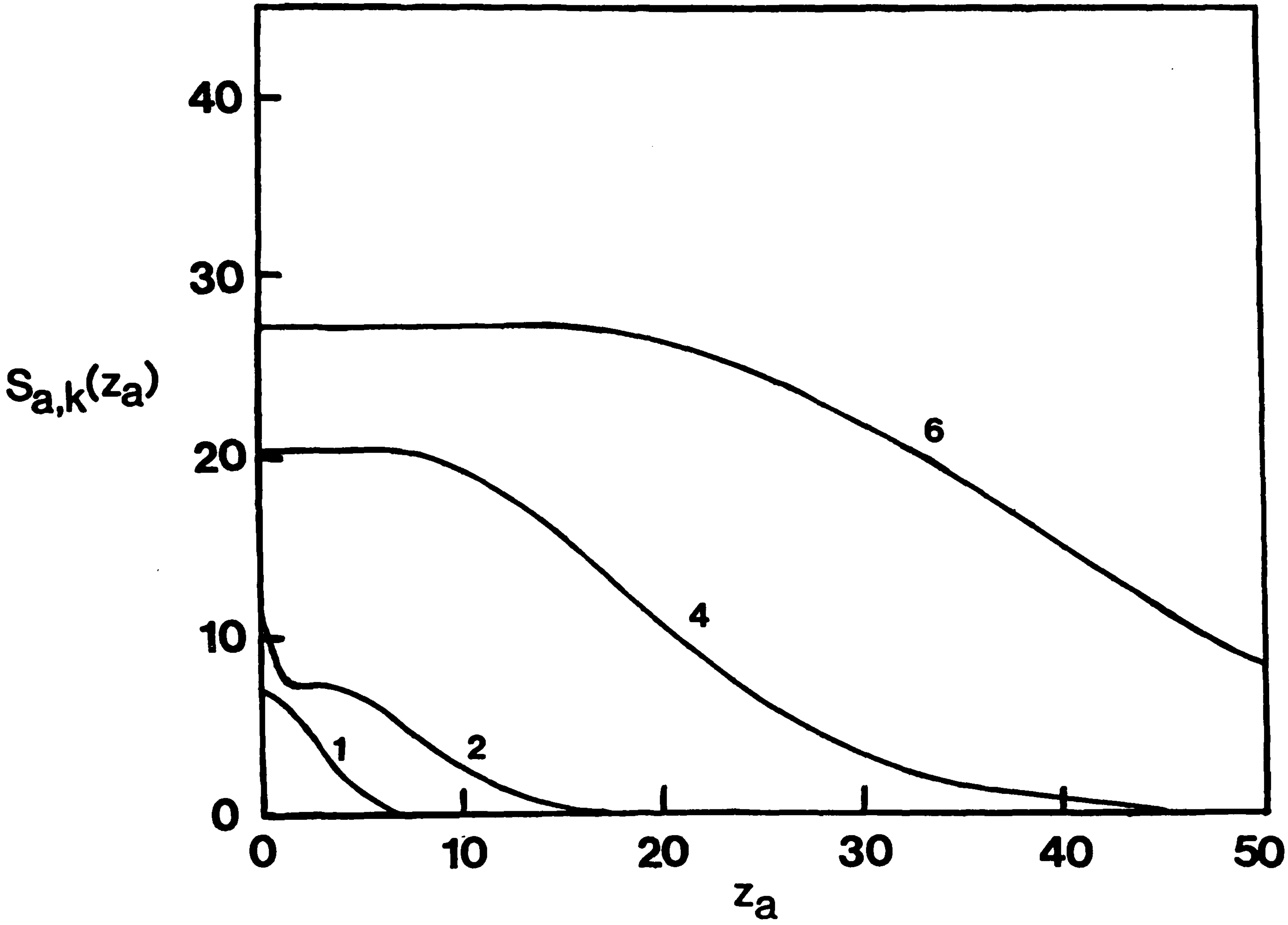
Figure Caption

1. The overlap $S_{a,z}(z_a)$ in units of the normalization factor, $(2/LA_s)^{1/2}$ versus the distance from the surface, z_a, in atomic units. The data are for hydrogen s orbitals overlapping the Fermi wavefunction of aluminum. The curves are labelled by the principal quantum numbers.



40
30
20
10
0
$S_{a,k}(z_a)$
6
4
2
1
0
10
20
30
40
50
z_a

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